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(54) **Method of manufacturing an improved fine-grained WC-Co cemented carbide**

(57) The present invention relates to a method of making a WC-Co-based cemented carbide with a fine WC-grain size. The cemented carbide is produced from well deagglomerated or easy to deagglomerate WC powder with round morphology, a Co powder also well deagglomerated or easy to deagglomerate and with a grain size equal to or smaller than the WC grain size and grain growth inhibitors. According to the invention the metal part of the grain growth inhibitors is added as part of the binder phase i.e. is included in the Co powder and alloyed therewith.

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## Description

[0001] The present invention relates to an improved method of making fine-grained WC-Co cemented carbide.

[0002] Cemented carbides for metal cutting have been used for almost 70 years. All the time improvements have been made and higher productivity has been achieved. One of the biggest inventions in this area was the coatings with thin layers of TiC, TiN,  $Al_2O_3$  etc., which have increased the metal removal rate considerably. The coatings have also been developed from the initial high temperature chemical vapour deposition (HT-CVD) towards lower deposition temperature (MT-CVD) and also Physical Vapour Deposition (PVD). The thickness and the adherence of the coatings have been improved as well which have changed the compositions for the cemented carbide substrates. Previously these substrates were more cutting tool materials than today when they are often just substrates adapted for optimum performance when combined with a coating. When the coating is worn through the cutting edge is changed.

[0003] Substrate development has included reducing the content of cubic carbides in the WC-Co-based cemented carbide substrates. These developments lead to a demand for finer WC grain size in the sintered cemented carbide than previously.

[0004] Extremely fine-grained WC-Co cemented carbides have been developed for drilling of composite printed circuit boards and similar applications. Here not only submicron but also so-called 'nano-sized' materials are available. The limit for 'nano-sized' is not defined in detail, but often up to 200 nm (0.2  $\mu m$ ) is considered as nano-size. Special production methods are used for these types of material.

[0005] The present invention relates to WC-Co-based cemented carbides produced from raw materials made via 'traditional' ways, i.e. tungsten carbide powder produced separately by carburizing tungsten metal powder or tungsten oxide with carbon and cobalt powder. Gas carburizing is of course included. The precipitation of a cobalt salt on the surface of tungsten carbide followed by reduction to metallic cobalt is consequently excluded.

[0006] The sintered WC mean grain sizes for alloys with improved properties if produced via the present invention are in the area 0.6-1.6  $\mu m$ , preferably 0.6-1.4  $\mu m$ . Also 0.4  $\mu m$  WC alloys can advantageously be produced this way but here there are not so many applications for ordinary metal cutting so far.

[0007] For submicron material grain growth inhibitors are used as a rule:  $Cr_3C_2$  and/or combinations of VC+ $Cr_3C_2$  are used for finer grain sizes.

[0008] All cubic carbides in Groups IV and V of the periodic table act as grain growth inhibitors for WC-Co-alloys: TiC, ZrC, HfC, VC, NbC, TaC but also the hexagonal  $Mo_2C$  and the orthorhombic  $Cr_3C_2$  of Group VI. For

WC-Co-alloys with a sintered mean grain size of 1.0-1.6  $\mu m$  for the tungsten carbide, TaC is a very common grain size stabilizer/grain growth inhibitor, but also NbC is used often in combination with TaC.  $Mo_2C$  can be used as well, both in the submicron and micron grain size area (0.8-1.6  $\mu m$ ).

[0009] The traditional way to produce cemented carbide is to wet mill the desired proportions of WC, Co and grain growth inhibitors, if any, and pressing agent like PEG or A-wax, in a ball mill with milling bodies of WC-Co (in order to avoid unwanted impurities in the material) extensively in alcohol/water or any other milling liquid. The final grain size of the tungsten carbide is determined during this process. The tungsten carbide is often strongly agglomerated and this is also valid for the cobalt powder. The milling process is often very long in order to:

1. Determine the final grain size of the tungsten carbide.
2. Get an even dispersion of the grain growth inhibitors to avoid grain growth in any part.
3. Have the cobalt evenly dispersed to avoid porosity and cobalt lakes in the sintered material.

[0010] This long milling time is detrimental to:

- 1) Wear of the milling bodies
- 2) Wear of the inner walls of the mills (high maintenance cost)
- 3) Investment costs in a lot of mills to produce the wanted amount of material

[0011] A long milling time will also create a very wide distribution in grain size of the milled WC particles. The numerous consequences of this broad distribution include: high compaction pressure with high deflection at unloading of the punch and high risk for cracks with modern complex geometries and the formation of unfavourable morphologies of the sintered WC grains (triangular, prismatic etc) resulting in low toughness (transverse rupture strength).

[0012] After milling, the slurry must be dried, often in a spraydrier, to get a free-flowing powder. This powder is then pressed and sintered to blanks followed by grinding to the final dimensions and often coated.

[0013] The object of the present invention is to avoid the production disadvantages described above and also to increase the performance level for the sintered material, mainly the toughness.

[0014] The invention consists of the following basic concepts:

- A well defined, narrow grain size distributed WC raw material with rounded morphology is used in which its final (sintered) grain size is already determined when it is produced via reduction and carburization. The WC must be deagglomerated into

single grains or be easy to deagglomerate. If a cemented carbide with a sintered WC mean grain size of 1.3  $\mu\text{m}$  is wanted the original WC must have a mean grain size of about (1.0-) 1.2  $\mu\text{m}$  because a certain small, but controlled, grain growth can never be avoided.

A well defined, narrow grain sized Co raw material, also with rounded morphology and with a mean grain size equivalent to or smaller than the mean WC grain size with which it will be mixed is selected. The cobalt powder must also be easy to deagglomerate. Advantageously, this Co raw material already includes at least the metal part of the grain growth inhibitors, i.e. the addition of the grain growth inhibitor is part of the Co powder production process. This means that also the cobalt is 'tailor made' for the final sintered alloy, because the amount and type of grain growth inhibitor additions are dependent on both final (sintered) WC grain size and the amount of binder phase desired.

A short milling time which is rather a blending and mixing than a traditional milling.

[0015] The use of the concepts listed above gives a cemented carbide with better production economy combined with better compacting properties (less cracks and better tolerances i.e. better shape stability) and increased toughness. The toughness increase is due to a better morphology with more rounded and less triangular and prismatic WC grains. With the grain growth inhibitors present where they are wanted/needed, i.e. the contact surfaces between Co and WC, the amount of grain growth inhibitors can often be decreased. Because these inhibitors, especially VC, are well known to decrease the toughness, a decrease of these elements but still the same effect because they are placed where they are needed, a better toughness can be obtained.

[0016] The invention is suitable for additions of up to 3, preferably up to 2, weight-% of V and/or Cr, Ti and Ta and/or Nb.

#### EXAMPLE 1

[0017] Two powder batches were produced, one according to established technology and one according to the invention.

##### Known technique:

[0018]

89.5 w/o WC, 0.8  $\mu\text{m}$  (FSSS)  
10.0 w/o Co standard (1.5  $\mu\text{m}$ )  
0.5 w/o  $\text{Cr}_3\text{C}_2$   
Milling time: 30 h

##### Invention:

[0019]

89.5 w/o WC, 0.70  $\mu\text{m}$  (FSSS)  
10.43 w/o Co-Cr (0.65  $\mu\text{m}$ )  
0.07 w/o C (carbon compensation)  
Milling time: 3 h

[0020] The Co-Cr alloy according to the invention contains Co and Cr in the proportions 10/0.43 and is easy to deagglomerate as well as the WC according to the invention.

[0021] The mills were identical as well as the total amount of powder in the mills. The slurries were spray dried with the same process parameters.

[0022] The two powders were pressed to insert blanks, SNUN 120308, in tools for 18% shrinkage when sintering.

[0023] The compacting pressure was 145 MPa for the powder produced according to existing technique and 110 MPa for powder according to the invention.

[0024] Desired compacting pressure is 100 $\pm$ 20 MPa.

[0025] The pressed compacts were then sintered in the same batch and had the same hardness in as-sintered condition, 1600 $\pm$ 25 HV3.

#### EXAMPLE 2

[0026] Of the same powders as in example 1, test pieces 5.5x6.5x21 mm were produced. They were sintered together and then tested in a 3-point bending test with the following results, mean values:

Known technique	Invention
2725 $\pm$ 300 MPa	3250 $\pm$ 200 MPa

#### EXAMPLE 3

[0027] Two alloys with the same composition were made, one according to the present invention and one according to known technique.

##### Known technique

[0028]

93.5 w/o WC 1.2  $\mu\text{m}$  FSSS  
6.0 w/o Co standard (1.5  $\mu\text{m}$ )  
0.5 w/o TaC  
Milling time: 40 h

Invention

[0029]

93.5 w/o WC      1.0  $\mu\text{m}$  (FSSS) 5  
6.4 w/o Co-Ta 0.8  $\mu\text{m}$   
0.1 w/o C (carbon compensation)  
Milling time: 4 h

[0030] The two variants were produced according 10  
to example 1. When pressing the same test inserts,  
SNUN 120308, the compacting pressure for 18%  
shrinkage was 160 MPa for the powder according to  
existing technique and 115 MPa for the powder accord- 15  
ing to the invention. After sintering both variants had the  
same hardness,  $1750 \pm 25$  HV3.

## Claims

1. Method of making a WC-Co-based cemented car- 20  
bide with a fine WC grain size using at least one  
grain growth inhibitor by mixing a well deagglomer-  
ated or easy to deagglomerate WC powder with  
round morphology, a Co powder also well deag-  
glomerated or easy to deagglomerate character- 25  
ised in that said at least one grain growth inhibitor  
is added as part of the Co powder i.e. is included in  
the Co powder and alloyed therewith.
2. Method according to claim 1 characterised in that 30  
the Co-powder has a mean grain size equal to or  
smaller than the WC-powder mean grain size.
3. Method according to any of the preceding claims 35  
characterised in that the sintered mean WC grain  
size is 0.6-1.4  $\mu\text{m}$ .

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